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Solubility and stability of scorodite, $FeAsO_4 \cdot 2H_2O$: Reply

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The discussions by Nordstrom and Parks (1987) and Robins (1987) enumerate some of the pitfalls (real and prospective) that might be encountered in experiments to measure the solubility of the mineral scorodite. In this reply, we present our opinions of the relative dangers of these various pitfalls and the values of the avoidance strategies proposed by Nordstrom and Parks (1987). In addition, we present an explanation for the failure of ferric hydroxide to nucleate in our experiments, and after a detailed analysis, we conclude that the solubility product of scorodite determined by Dove and Rimstidt (1985) and Robins (1987) is the best value currently available and is sufficiently accurate for most geochemical applications.

Nordstrom and Parks begin with a list of criteria that they believe are required for a "successful" solubility measurement. We shall comment on these in the order in which they were presented.

1. Although demonstrating the reversibility of a reaction is desirable in some cases, it is often not practical and certainly not required in order to obtain reasonable and useful thermodynamic values. For example, no measurements of amorphous silica solubility have been reversed, yet the published values are widely accepted and utilized. In addition, almost none of the reported quartz solubility values come from reversed reactions; in fact, the data from the only comprehensive attempt to measure quartz solubilities by reversing the reaction (Crerar and Anderson, 1971) were discounted in favor of unreversed measurements in the reviews of quartz solubility by Fournier (1979) and Fournier and Potter (1982).

2. We determined the stoichiometry of the reaction that we studied by measuring the pH along with the Fe^{3+} and the arsenate concentration in the solution. The equal molal concentrations of Fe and arsenate in solution demonstrate that the scorodite sample dissolved congruently, and the lack of a shift to a lower pH shows that there was no significant ferric hydroxide precipitation (this point will be discussed in detail in a later section). The technique of varying the concentration of one or more aqueous species described by Nordstrom and Parks is commonly used to determine the stoichiometry of aqueous complexes (see for example, Barnes, 1981). However, if the stability and stoichiometry of the aqueous species are known, as in this case, this approach is redundant.

3. Although it is usually not possible to really identify all possible reactions in a system such as this where the thermodynamic database is relatively sparse, we feel that we have considered the most pertinent reactions in our study, i.e., the congruent-dissolution reaction and the incongruent-dissolution reaction that precipitates ferric hydroxide. By choosing experiments that showed no evidence of iron hydroxide precipitation, we were able to determine the solubility product for the congruent, but metastable, reaction.

4. We demonstrated that the material that we used in our experiments was well-crystallized scorodite by using both X-ray diffraction analysis and light-microscope observations. Although it is true that X-ray diffraction seldom detects phases present in amounts of less than 5%, light microscopy can detect amounts of less than 1%.

5. The sampling and analytical procedures that we used are quite standard, and we are unaware of any problems with them.

6. The problem of converting solubility measurements to equilibrium constants expressed in terms of an infinite dilution reference state is formidable. At the present time, there is no general model of electrolyte solutions that reliably predicts activity coefficients for species in complex solutions at concentrations above about 0.1m (molal). Computer models such as WATEQ and MINEQL are quite useful for general modeling of natural systems where order-of-magnitude results allow reasonable geochemical interpretations, but they use a variety of undocumented data and algorithms, making them inappropriate vehicles for data reduction. Furthermore, none of these models allows for the propagation of errors through the calculation, and therefore the uncertainty of the calculated equilibrium constant(s) cannot be ascertained. Thus, as we pointed out in our reply to Robins (Dove and Rimstidt, 1987), we chose to avoid all of these difficulties by performing our measurements under very low ionic strength conditions where such detailed modeling is unnecessary.

Nordstrom and Parks suggest that for this system "the best chance of simple interpretable behavior would be under strong acid conditions." There are at least two reasons why this is not true. First, it is very likely that scorodite is unstable (metastable) at pH <2 and would break down to form $As_2O_{5(s)}$ and Fe^{3+} (based on the ΔG_f of $As_2O_{5(s)}$ given by Naumov et al., 1974). The stability field of this phase is shown in Figure 6 in Dove and Rimstidt (1985). Second, strongly acid solutions would have high ionic strengths and moderately high concentrations of species (including, perhaps, the anion from the acid used

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to titrate the solution to low pH) that could form complexes and ion pairs with each other, so that determining a solubility product based on an infinitely dilute reference state from concentration measurements for such a solution is a nearly impossible task.

We agree with Nordstrom and Parks that there are only three pertinent studies of scorodite: Chukhlantsev (1956), Robins (1987), and Dove and Rimstidt (1985). Attempts to measure the equilibrium solubility starting from extreme supersaturations (e.g., Hartshorn, 1927) are generally confounded by the formation of metastable phases. This may also be true for the experiments of Chukhlantsev (1956) and might be an alternative explanation (to our particle size argument) for the fact that his reported solubility product is larger than the others. It is true that rapid mixing of Fe^{3+} and arsenate solutions to form a very supersaturated solution is likely to produce metastable phases and very small particles containing occluded water that might require some time to recrystallize to form scorodite. However, we feel that the statement of Nordstrom and Parks that "this system reaches equilibrium with extreme difficulty, and that formation of additional complex solids and aqueous species is quite likely" is a gross overgeneralization. We found that we could produce synthetic scorodite with no difficulty using the technique outlined in Dove (1984). Furthermore, because our experiments involved the dissolution of well-crystallized scorodite, rather than precipitation of scorodite, this discussion is irrelevant to our results. Our experiments suggest that equilibration times of only several days are required for reliable solubility measurements. Table 2 in Dove and Rimstidt (1985) shows that the solubility products calculated from identical runs at 5, 8, 25, and 57 d were essentially the same, indicating that these runs all reached equilibrium in less than 5 d.

Nordstrom and Parks and Robins suggest two scenarios in which the formation of ferric hydroxide precipitates could have distorted our results. In the first one, ferric hydroxide microparticles (it is not clear whether these are colloids or large polymers) form in the solution, lowering the activity of Fe^{3+}, and leading to further dissolution of scorodite. We are unaware of any documentation of ferric hydroxide microparticles in the literature. Such an ad hoc hypothesis is somewhat akin to the notorious "hidden pluton at depth" model for the source of many ore deposits. It is easy to propose, but very difficult to disprove because the culprit is hidden from view. However, the most sensitive way to detect the precipitation of ferric hydroxides is to monitor the pH of the solution. If scorodite dissolves incongruently according to Equation 4 given in Dove and Rimstidt (1985), $FeAsO_4 \cdot 2H_2O + H_2O = H_2AsO_4^- + Fe(OH)_{3(s)} + H^+$, then the pH of the solution should decrease as a result of the H ions produced by ferric hydroxide precipitation. Such a pH decrease is quite evident when this reaction occurs, as is shown in Figure 3 in Dove and Rimstidt (1985), but there was no shift toward lower pH in the four experiments that we assert were congruent (note the *final* pH column in Table 2, Dove and Rimstidt, 1985). The second scenario proposed by Nordstrom and Parks and by Robins involves the formation of a coating of ferric hydroxide on the surface of the dissolving scorodite particles. In order for such a coating to significantly affect the rate of dissolution of the scorodite grains, it would necessarily be continuous and thick. If such a thick and continuous layer of ferric hydroxides coated the grains, they should have a "reddish-brown" color characteristic of ferric hydroxides (Robins, 1987). After our experiments were complete, the run solids were the near-white color of scorodite and showed no evidence of Fe staining. In addition, if a significant amount of Fe were removed from solution by the formation of such a coating, the Fe concentration in the solution would have been considerably lower than the arsenate concentration and the pH would have shifted to a lower value as described above. We have verified that in the four experiments from which we obtained our published solubility product, the Fe and arsenate concentrations were nearly equal, and the pH was essentially constant (Table 2 in Dove and Rimstidt, 1985).

There is no doubt that the four solutions that we analyzed to determine the solubility product of scorodite were quite supersaturated with respect to ferric hydroxide, and in fact, this seems to be the real concern of Nordstrom and Parks and of Robins. They deal with this observation by denying that it is possible, but perhaps it offers an important clue about the behavior of the iron arsenate system. We feel that a more plausible explanation of the failure of ferric hydroxides to nucleate and grow in some of our experiments is that moderate concentrations of arsenate poisoned their growth. There is a lot of circumstantial evidence to support this hypothesis. First, arsenate strongly adsorbs to the surface of ferric hydroxide (Pierce and Moore, 1982). The presence of arsenate on the surface of iron hydroxides could block further growth, much as adsorbed Mg ion blocks the growth of calcite and leads the precipitation of metastable aragonite. Because the amount of arsenate adsorbed increases with increasing pH, this inhibiting effect would be greater at high pH values. Second, iron hydroxides are present, but not abundant, in the waste piles at the Brinton arsenic mine (see Dove and Rimstidt, 1985), even though scorodite has been exposed there for the past 60+ years. During that time, a substantial amount of scorodite must have dissolved, and yet the surfaces of the exposed scorodite retain the characteristic greenish-white color of scorodite and are not Fe stained. This suggests that the growth of iron hydroxides is inhibited in natural settings as well as in experiments. Third, this would explain why ferric hydroxides are not formed in great abundance at the time that arsenopyrite oxidizes to form natural scorodite. Our measurements of the pH of solutions escaping from waste piles at the Brinton arsenic mine, where arsenopyrite is currently oxidizing to form scorodite, show values ranging from 4.2 to 5.8. These values are significantly higher than commonly found for acid mine drainage where pyrite is oxidizing. We suspect that these higher pH values are characteristic of places where arsenopyrite is oxidizing in the absence of other sulfide minerals, because most of the ferric iron produced by arsenopyrite oxidation is used to form scorodite rather than hydrolyzing to form ferric hydroxide and H ions. Thus, arsenopyrite oxidation produces much less acid than pyrite oxidation, and scorodite formation likely occurs at pH values between 3 and 6. Under these conditions, ferric hydroxides should form rather than scorodite, but as we previously stated, they are not common, presumably because their growth is inhibited by the arsenate-rich solutions. Fourth, the experiments that we began at pH = 10.4 and pH = 3.1 all eventually precipitated some ferric hydroxides according to Equation 4 given in Dove and Rimstidt (1985); $FeAsO_4 \cdot 2H_2O + H_2O = H_2AsO_4^- + Fe(OH)_{3(s)} + H^+$. The equilibrium constant for this reaction can be estimated to be $\sim 10^{-6.6}$ by using our solubility product for scorodite and the hydrolysis constants given in Table 1 of Dove and Rimstidt (1985) and by assuming that the ferric hydroxide precipitated had a solubility product of $10^{-38.6}$. This means that the pH of a dilute solution equilibrated with scorodite and ferric hydroxide should be near 3.4. The experiments begun at pH = 3.1 eventually reached pH values of 3.43 (42 d) and 3.39 (52 d) (see Fig. 3, Dove and Rimstidt, 1985), suggesting that at low pH where arsenate does not adsorb as strongly to the growing ferric hydroxide particles, the system can reach the equilibrium described by this reaction. In addition, these solutions had time to equilibrate with both ferric hydroxides and scorodite, so the system was at a $Fe(OH)_3$-scorodite-solution invariant point similar to the one shown on Figure 1 in Dove and Rimstidt (1987), but shifted to a lower pH because the ferric hydroxide actually formed was more stable than the one assumed for the calculation of the diagram. If this interpretation is correct, it should be possible to calculate the solubility product of scorodite, based on the congruent-solution reaction, from the composition of these solutions. These calculated solubility products of $10^{-21.9}$ (43 d) and $10^{-21.5}$ (52 d) (Dove, 1984; App. VII) are in excellent agreement with our published value of $10^{-21.7 \pm 0.5}$. On the other hand, the experiment begun at pH 10.4 initially precipitated iron hydroxide, as expected, causing the pH to shift to lower values (see Fig. 3, Dove and Rimstidt, 1985), but this reaction was arrested by the time the solution reached pH ≈ 6. At these higher pH values, arsenate adsorbed strongly enough onto the growing ferric hydroxide particles to restrict further growth, so the incongruent reaction was poisoned and the solution pH remained near 6 rather than continuing to drift downward toward the equilibrium pH of ~3.4. It is interesting to note that the solubility product calculated from the 52-d experiment in this series is $10^{-21.4}$ (Dove, 1984; App. VII), showing very close agreement with our reported value of $10^{-21.7 \pm 0.5}$ for congruent dissolution. This suggests that after the incongruent-dissolution reaction was poisoned by arsenate adsorption on the ferric hydroxides, the solution was forced to equilibrate with the scorodite via the congruent reaction. Thus there is good evidence that adsorbed arsenate poisons the growth of ferric hydroxides at high pH values so the incongruent-reaction path is blocked and the system is forced to equilibrate with scorodite by the congruent reaction. Finally, we conclude that, for our four experiments that showed congruent dissolution, the scorodite dissolved quickly enough to generate the moderate concentration of arsenate necessary to poison the nucleation and growth of ferric hydroxides, and therefore these experiments were forced to follow the path of congruent dissolution.

We reiterate here that we agree completely with Robins (1987) and Nordstrom and Parks (1987) that according to equilibrium thermodynamics, ferric hydroxides should have precipitated in all of our experiments including the four that showed congruent dissolution. The fact that we found equivalent amounts of Fe^{3+} and arsenate in the solutions, observed no color change of the run solids (red-brown ion hydroxide), and saw no shift to lower pH argues that the reactions in these experiments actually were congruent. In addition, the solubility product from these four experiments agrees well with the one reported by Robins (1987), with the values estimated from the experiments of Nishimura and Tozawa (1978) by Nordstrom and Parks (1987), and with the values estimated from our experiment in which incongruent dissolution took place. Because of the quite different conditions of these various experiments, we feel that this coincidence of results is not fortuitous but rather is evidence that our model of scorodite solubility and inhibition of ferric hydroxide formation by arsenate is robust and that the solubility product that we reported (Dove and Rimstidt, 1985) is completely valid.

We did not give the free energy of formation of Fe^{3+} that we used to calculate the free energy of formation of scorodite. We apologize for this oversight; we used $\Delta G_f^0(Fe^{3+}) = -16.95$ kJ·mol^{-1} (Dove, 1984).

We thank Nordstrom, Parks, and Robins for their interest in our paper and hope that this reply to their questions creates some enlightenment.

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REFERENCES

Barnes, H.L. (1981) Measuring thermodynamically-interpretable solubilities at high pressures and temperatures. Physics and Chemistry of the Earth, 13 and 14, 321–338.

Chukhlantsev, V.G. (1956) The solubility products of a series of arsenates. Zhurnal Analitichesikoi Khimii, 11, 565–571.

Crerar, D.A., and Anderson, G.M. (1971) Solubility and solvation reactions of quartz in dilute hydrothermal solutions. Chemical Geology, 8, 107–122.

Dove, P.M. (1984) The solubility and stability of scorodite, $FeAsO_4 \cdot 2H_2O$. M.S. thesis, Virginia Polytechnic Institute and State University, Blacksburg, Virginia.

Dove, P.M., and Rimstidt, J.D. (1985) The solubility and stability of scorodite, $FeAsO_4 \cdot 2H_2O$. American Mineralogist, 70, 838–844.

——— (1987) Solubility and stability of scorodite, $FeAsO_4 \cdot 2H_2O$: Reply. American Mineralogist, 72, 845–848.

Fournier, R.O. (1979) Discussion: Calculation of the thermodynamic properties of aqueous silica and the solubility of quartz and its polymorphs at high pressures and temperatures. American Journal of Science, 279, 1070–1082.

Fournier, R.O., and Potter, R.W., II. (1982) An equation correlating the solubility of quartz in water from 25° to 900°C at pressures up to 10,000 bars. Geochimica et Cosmochimica Acta, 46, 1969–1973.

Hartshorne, N.H. (1927) The system ferric oxide–arsenic acid–water at low concentrations of arsenic acid. Journal of the Chemical Society (London), 2, 1759–1768.

Naumov, G.B., Rhzhenko, B.N., and Khodakovsky, I.L. (1974) Handbook of thermodynamic data. NTIS Report No. USGS-WRD-74-001, 328 p.

Nishimura, T., and Tozawa, K. (1978) On the solubility products of ferric, calcium and magnesium arsenates. Bulletin of the Research Institute of Mineral Dressing and Metallurgy (Tohoku University), 34, 20–26 (in Japanese).

Nordstrom, D.K., and Parks G.A. (1987) Solubility and stability of scorodite, $FeAsO_4 \cdot 2H_2O$: Discussion. American Mineralogist, 72, 849–851.

Pierce, M., and Moore, C.B. (1982) Adsorption of arsenite and arsenate on amorphous iron hydroxide. Water Resources, 16, 1247–1253.

Robins, R.G. (1987) Solubility and stability of scorodite, $FeAsO_4 \cdot 2H_2O$: Discussion. American Mineralogist, 72, 842–844.

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